# **Vapour Phase Thermal Conductivity Measurements of Refrigerants**

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<sup>1</sup>Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A.

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### ABSTRACT

The paper reports further developments of the transient hot-wire technique. The particular development of interest is the extension of the technique to study polar, or electrically-conducting gases with a relatively low thermal conductivity but a high thermal diffusivity, circumstances which occur at low density and, therefore pressure, for gases of high molecular weight.

The theory of the transient hot-wire instrument is examined again in order to guide a revised design of the thermal conductivity cell with this particular application in mind. Test measurements have then been conducted on helium, argon and propane at low and moderate pressures to confirm that the instrument operates in accordance with the theory of it.

The satisfactory completion of these tests demonstrates that the new equipment overcomes many of the defects observed in earlier variants of the instrument for application to the study of refrigerant gases.

KEY WORDS: argon; experimental method; helium; low density; propane; thermal conductivity.

#### 1. INTRODUCTION

In an earlier paper [1] we considered the application of an existing transient hotwire instrument for the measurement of the thermal conductivity of gases to the study of refrigerants. The motivation for that earlier study, as well as for the present one, was to seek a method for the measurement of the thermal conductivity of such gases, which are generally polar, and frequently seem not to be complete electrical insulators [2]. The total range of pressures accessible to the usual instrument for such gases is very restricted, particularly at low temperatures [3].

Our initial study [1] concentrated on ways to decrease the lower pressure (density) limit for operation of a transient hot-wire cell for simple gases such as nitrogen and argon. It was concluded that a hot-wire cell with a bare platinum wire of 7 mm diameter should be employed and that measurements at short times only should be used.

In this work we have considered the same problem afresh, recognising that if it is intended to study polar refrigerants with a similar experimental technique, then it is best to use an insulated hot wire [2]. Unfortunately, the smallest diameter of metallic wire that can be insulated with a non-interfering film, and is commercially available, is wire made of tantalum with a nominal diameter of 25 mm [3]. If this is employed in the same cell as described above, it follows that the heat capacity correction at short times will be a factor of 16 times larger than for the platinum wire. In consequence, unless there is careful design, there may be no time available during a transient run in which neither heat capacity nor outer boundary corrections are very small. The measurement of the thermal conductivity is then rendered impractical. Here we describe a means to escape from this difficulty and demonstrate the viability of a revised experimental installation.

### 2. CELL DESIGN

The fundamental theory of the transient hot-wire technique is described in detail in reference [3]. For the current purpose it is sufficient to record that the measured transient response,  $DT_w$ , of the temperature of a finite segment of an insulated metallic wire (radius a) immersed in a fluid following initiation of a heat flux, q, within it conforms to the equation

$$DT_{id} = DT_{w} + \sum_{i} dT_{i} = \frac{q}{4pl} \ln \frac{4kt}{a^{2}C}$$
 (1)

Here  $dT_i$  represents one of a series of corrections that describe the departure of the real cell from an ideal cell. We concentrate only upon the two corrections that are germane to the arguments presented in the paper. There is ample evidence that the remainder of the corrections, and their current method of application, such as those involving the presence of a thin insulating layer [4], are entirely adequate for accurate measurements [3].

The heat capacity correction,  $dT_i$ , is most often used in an approximate form derived by Healy *et al.* [5]. For the circumstances to be considered here the approximation used by Healy *et al.* is inappropriate and we therefore use the full form of the correction [6]

$$dT_{1} = \frac{q}{4pl} \left[ \ln \frac{4kt}{a^{2}c} - \frac{16ql^{2}k}{p^{2}a^{3}} \int_{0}^{\infty} \frac{1 - e^{-k_{w}u^{2}t} J_{o}(ur) J_{1}(ua)}{u^{4} [j^{2}(u) + y^{2}(u)]} du \right]$$
(2)

Here,

$$j(u) = \int_{w}^{1} k^{\frac{1}{2}} J_{1}(au) J_{0}(\sqrt{k_{w}/k} au) - \int_{w}^{1} k^{\frac{1}{2}} J_{0}(au) J_{1}(\sqrt{k_{w}/k} au)$$
(3)

and

$$y(u) = \int_{w}^{1} k^{\frac{1}{2}} J_{1}(au) J_{0}(\sqrt{k_{w}/k} au) - \int_{w}^{1} k^{\frac{1}{2}} J_{0}(au) J_{1}(\sqrt{k_{w}/k} au)$$
(4)

In addition, I signifies the thermal conductivity, k the thermal diffusivity and the subscript w refers to properties of the wire. Finally,  $J_0$  and  $J_1$  are Bessel Functions.

The outer boundary correction,  $dT_2$ , is given by [5]

$$dT_2 = \frac{q}{4pl} \left\{ \ln \frac{4kt}{b^2 C} + \sum_{n=1}^{\infty} e^{-g_n^2 kt/b^2} [pY_0(g_n)]^2 \right\}$$
 (5)

where b is the radius of the cylindrical surface surrounding the fluid which is assumed to remain at the constant equilibrium temperature of the cell during a transient run.

Both corrections  $dT_1$  and  $dT_2$  can be expressed as functions of three reduced variables for convenience of exposition; they are  $t^* = kt/a^2$ ,  $h^* = (\Gamma C_p)_w/\Gamma C_p$  and  $r^* = b/a$ . Figures 1(a) and 1(b) illustrate the magnitudes of the two corrections for a variety of values of  $h^*$ , typical of a range of gases at 0.1 MPa and 300 K and for a typical series of ratios b/a. It can be seen that, for a particular fluid diffusivity, decreasing the reduced time  $t^*$  but increasing the radius of the wire dramatically increases the magnitude of the heat capacity correction. On the other hand, as Figure 1(b) reveals, if we increase a and b so as to keep  $r^*$  constant, then the change in the outer boundary correction takes place along one of the lines of constant  $r^*$  in the figure and necessarily decreases as  $t^*$  is

reduced. The implication of these results is that if we can tolerate and evaluate with sufficient accuracy a large heat capacity correction, we can reduce the outer boundary correction to negligible proportions by allowing  $r^*$  to increase by using a larger value of b. This means that a possible design of thermal conductivity cell for the conditions of interest should make use of a larger wire diameter **and** a larger cell diameter than in our previous designs [3]. Such a design would allow operation at low gas densities and high gas thermal diffusivities without the need to reduce the upper time limit of measurement to unacceptable limits.

### 3. EXPERIMENT

A transient hot-wire cell has been constructed guided by the principles set out in the previous section. A brief description of the essential features of the cell is given here although more details will be provided later [7]. The two hot wires themselves are made of 25 mm diameter tantalum wire. The long wire has a length of approximately 150 mm and the short wire 50 mm. Each wire is mounted on the axis of a separate cylindrical, vertical tube of radius 79 mm. The wires are tensioned by an insulated cantilever spring arrangement at the top of each tube mounted on the top plate. The top and bottom fixtures of the wire are spot-welded and they are themselves connected to a tantalum support rod. These measures ensure that the transient thermal expansion of the hot wires during measurement is absorbed by the cantilever spring without introducing electrostrictive or thermal oscillations [8]. Furthermore, differential expansion of the wire supports and the wires at different equilibrium thermodynamic states that could introduce strains are avoided. The use of tantalum in the construction anticipates the

eventual use of the cells for measurements on electrically-conducting fluids since anodisation of the entire assembly *in situ* is straightforward [9].

A new electronic measurement system has been developed to take advantage of the most modern methods for determining the change of the resistance difference between the long and short tantalum wires during transient heating by the same current. Details of the bridge are beyond the scope of this paper but it suffices to say that the bridge permits 1000 measurements of the resistance change to be carried out in the time interval from 1 ms to 1 s. The resolution of the temperature rise measurements is estimated to be  $\pm$  0.1% and time is measured with a precision of  $\pm$  1 ms. The temperature coefficient of resistance for tantalum necessary for the analysis of the data was taken from the work of Assael *et al.* [10].

In order to confirm that the instrument described operates in accordance with the theory of it and, in particular, that the argument set out in favour of the use of larger wire diameters and large cell diameters is correct for work with low density gases, we have conducted a series of test measurements. To be specific, we have carried out measurements of the thermal conductivity of argon, helium and propane at pressures within the range 0.1 MPa to 8.0 MPa and temperatures in the range 305 K to 363 K. In the following section we consider the results which confirm correct operation of the instrument and report some new thermal conductivity data.

#### 4. **RESULTS**

## 4.1 Confirmation of the Operation of the Instrument

Figure 2 shows a plot of the deviations of experimental measurements of the temperature rise of the hot wires (in argon at 305 K at a pressure of 0.1 MPa) from a fit of  $DT_{expt}$  vs  $\ln t$  to the data for times in the range 100 ms to 1 s. Inset in the figure we show the magnitude of the heat capacity correction as a fraction of the temperature rise as a function of time. It can be see that, over the time interval 50 ms to 1 s, the behaviour of the corrected experimental data conforms to that predicted by equation (2). Given that at 50 ms the heat capacity correction in this case amounts to 63% of the temperature rise, this is an impressive demonstration of the degree of uniformity between the theoretical model of the experiment and reality.

In routine measurements, of course, it is neither necessary nor good practice to include points for transient runs in which the heat capacity correction, or any other, is so large that its evaluation may introduce errors into the corrected temperature rise that are larger than the random error of measurement. Thus, we routinely impose the condition that the estimated error in the heat capacity correction should not exceed 0.1% of the temperature rise and exclude all points from the fit (at short times) for which this condition is fulfilled. The evidence of the run contained in Figure 2 supports the fact that we may be able to evaluate the heat capacity correction to within  $\pm$  2% so that we routinely reject all points in transient runs for which the heat capacity correction exceeds 5% of the temperature rise.

Figures 3(a)-(c) show the deviations of the results of transient temperature rise measurements in argon at 505 MPa and 333 K (a), in helium at 1.0 MPa and 365 K (b),

and in propane at 0.1 MPa and 333 K (c) for fits linear in ln *t* over the time range determined in this fashion.

In no case is there any evidence of systematic curvature in a time range that for helium encompasses 30 ms to 1 s, while for propane it is restricted to 0.3 s to 1 s. This range of times is entirely adequate to obtain the slope of the line relating  $DT_{id}$  vs  $\ln t$  and evaluate the thermal conductivity of the fluid from equation (1).

The results presented in Figure 3 for low pressures are to be contrasted with those reported earlier [1] for a wire with a much smaller diameter in a smaller cell. The difficulties revealed in the earlier results, where at long times there was curvature of the plot of temperature rise against ln *t*, have been completely removed. This is attributed to the fact that for no case in the present work, even at the lowest pressure, did the outer boundary correction, even estimated approximately, exceed 0.8%.

### 4.2 Thermal Conductivity Data

Figure 4 presents a comparison of the present data for the thermal conductivity of argon at T=308.15 K and T=335.15 K with a correlation of them. The same figure includes comparison with the results of earlier work [11-14]. Figure 5 contains a similar comparison for helium at T=338.15 K. The deviations are at most  $\pm 0.5\%$  except for the lowest density points for helium reported by Mustafa *et al.* [14]. The fact that the present data extend smoothly to lower densities than hitherto is apparent.

A further test of the equipment for the monatomic gases is afforded by the Eucken relation which requires (according to rigorous theory) that for monatomic gases [15]

$$\frac{15}{4} \frac{1_{0} R \mathscr{F}}{\mathsf{h}_{0} M} = 1 \tag{6}$$

where  $I_0$  and  $h_0$  are the zero-density limits of the thermal conductivity and viscosity respectively and  $\mathcal{F}$  a higher-order Kinetic Theory correction factor. Using the best available viscosity data for helium and argon under the conditions of interest [16], and values of  $I_0$  deduced by statistical analysis of our data [17], we have evaluated the ratio on the LHS of equation (6). The results are contained in Table 1 and show that within  $\pm$  0.7% the theoretical result is attained. Accounting for errors in the viscosity data employed, this indicates that the error in the absolute thermal conductivity reported in the present work is one of  $\pm$  0.5%.

For propane there are no reliable data available for comparison in an overlapping range of temperature and pressure. We thus confine our comparison here to a report of the single value of  $\mathbb{I}_0$  so far obtained which is contained in Table I.

## 5. CONCLUSIONS

It has been shown that it is possible to design a transient hot-wire thermal conductivity apparatus to work at low densities for gases of low thermal conductivity and relatively high thermal diffusivity. This demonstration, conducted in an apparatus that can house electrically-insulated hot wires, opens the route to accurate measurements on the thermal conductivity of the vapour phase of new refrigerants under sub-critical conditions.

# **ACKNOWLEDGEMENTS**

S.H. Jawad gratefully acknowledges financial support from the Engineering and Physical Sciences Research Council.

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Table I

Optimum Values of Thermal Conductivity in the limit of zero-density and experimental

Euken factors

T	$\lambda_0 \pm \sigma_{\lambda 0}$	η <sub>0</sub> [16]	Eu*
(K)	$(mWm^{-1}K^{-1})$	(µPa.s)	
Argon			
308.15	$18.10 \pm 0.02$	23.24	0.998
335.15	$19.50 \pm 0.02$	24.81	1.007
Helium			
338.15	$168.92 \pm 0.03$	21.64	1.002
365.15	$179.15 \pm 0.06$	22.82	1.008
Propane			
355.15	$26.23 \pm 0.03$		

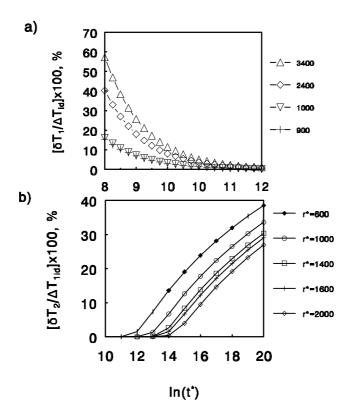
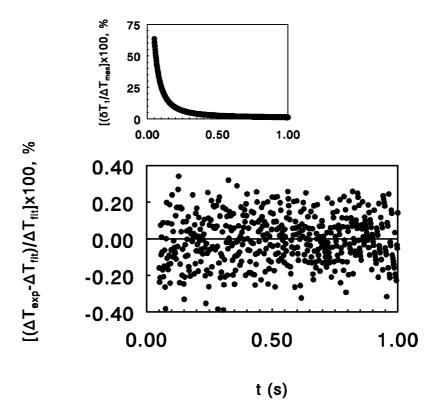


Fig 1.

- a) Fractional heat capacity correction for the transient hot-wire as a function of reduced time with the heat capacity per unit volume of ratio  $h^* = (r c_p)_w / r c_p$  as a parameter
- b) Outer boundary correction for th transient hot-wire as a function of reduced time with the radius ration  $r^*=b/a$  as a parameter.



**Fig. 2.** Deviation of the experimental temperature rise form a linear fit over the time range 50 ms to 1 s for argon at 308.15 K and 0.15 MPa (inset in the figure is the value of the heat capacity correction as a fraction of the measured temperature rise)

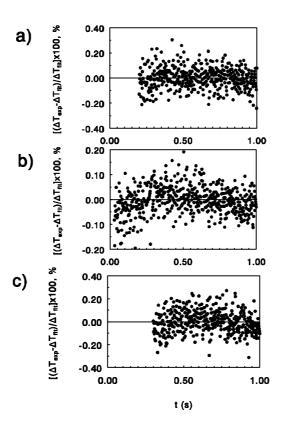
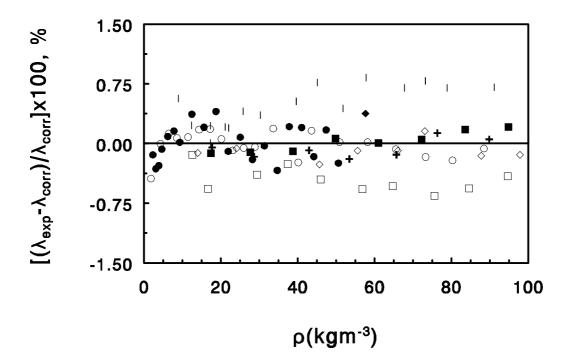


Fig. 3. Deviations of experimental temperature rise from a linear fit to it.

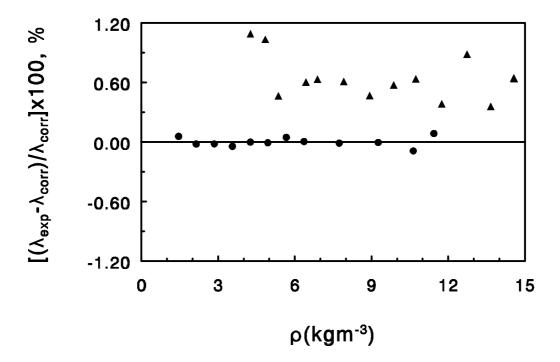
- a) Argon at 335.15 K and 5.5 MPa;
- b) Helium at 338.15K and 1.0 MPa;
- c) Propane at 355.15 K and 0.1 MPa;



**Fig. 4** Deviations of the thermal conductivity of Argon from the correlation of the present results,

● Present data 308.15 K; ■ 308.15 K [11]; **+** 308.15 K [12]; ◆ 308.15 K [13]

O Present data 335.15 K; ÿ 333.15 K [11]; ◊ 335.15 K [13]



**Fig. 5.** Deviations of the thermal conductivity of Helium from the correlation of the present results,

● Present data 338.15 K; ▲ 338.15 K [13]